



DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; TERRANOVA, ANDREW C. ET AL: "Effect of a chelating agent (EDTA) on the tobacco hornworm" retrieved from STN Database accession no. 73:74314 XP002265347 * abstract * & JOURNAL OF ECONOMIC ENTOMOLOGY (1970), 63(3), 886-91 ;	1-27	A01N25/00 A01N37/44 A01N59/00
X	EP 0 836 917 A (UPM-KYMMENE OY) 22 April 1998 (1998-04-22) * page 3, line 24 - line 36 *	1-27	TECHNICAL FIELDS SEARCHED (Int.Cl.7) A01N
X	US 3 786 079 A (TOYOZO YONEZAWA) 15 January 1974 (1974-01-15) * the whole document *	1,4-6, 16,17, 22-24	
X	GB 2 368 284 A (TROS PTY LTD) 1 May 2002 (2002-05-01) * page 3, line 11 - page 7, line 32 *	1-15	
X	WO 99 39576 A (W.NEUDORFF GMBH) 12 August 1999 (1999-08-12) the whole document	1-15	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 December 2003	Examiner Fort, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

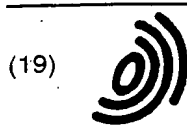
ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 03 02 1340

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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17-12-2003

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EP 0836917	A	22-04-1998	FI	964147 A	16-04-1998
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Europäisches Patentamt
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Office européen des brevets



(11) **EP 0 836 917 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
22.04.1998 Bulletin 1998/17

(51) Int Cl.⁶ **B27K 3/36, B27K 3/34**

(21) Application number: **97660107.0**

(22) Date of filing: **14.10.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**

(30) Priority: 15.10.1996 FI 964147

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(54) **Preservation of wood against insect damage**

(57) The invention relates to the use of an aminocarboxylic acid or aminocarboxylate in the preservation

of wood against attack from insects, particularly from termites of the *Coptotermes* family or the house long-horn (*Hyloterpes bajulus*).

EP 0 836 917 A1

Description

The present invention relates to the preservation of wood against damage caused by insects.

A plurality of different insect families such as beetle pests and termites can feed on wood thus causing extensive damage in structural timber. The damage is caused either so that the insects (or their larvae) consume wood as their nutrition, or alternatively, use the wooden material as their nesting environment. Insect attack will be evidenced in the wood as various gallery and bore patterns, whereby the wood utilized by the insects is converted into powdery frass. Typically, the strength properties of wood will degrade rapidly due to damage by insects.

In Finland, wood or wooden products need no separate preservation against insects, because here damage caused by insects is almost invariably associated by rot due to fungal attack. However, the situation is already entirely different with regard to Central and Southern Europe, where preservation of wood with the help of insecticides is a necessity. Insects causing damage to wood belong chiefly in these three major orders: *Isoptera*, *Coleoptera* and *Hymenoptera*. On a world-wide scale, damage from attack by insects is estimated to reach several billions of US dollars. Insects can attack living, standing wood, green felled wood, stored lumber and wood already installed in worked form (e.g., structural timber). Today, insects of different species cause extensive damage in Central and Southern Europe; in Finland insects occur as "secondary pests" only by attacking decaying wood predominantly.

Termites attacking wood belong to the order *Isoptera*. About 2000 different species are included in termites that occur principally in such climatic regions where the average annual temperature is at least 10 °C. Termites utilize the cellulosic component of wood which is decomposed by commensal microorganisms living in the gut of termites. Termites are divided into two major groups of which one is capable of degrading wood in contact with the ground or otherwise having a high moisture content, while the other group uses dry wood (moisture content below 13 %). In Europe, termites can be found chiefly in the southern part of Europe (e.g., in Portugal and Southern France), while local occurrence farther north is also known (e.g., in Hamburg). The termite species occurring in Europe are those favouring moist wood, whereby damage caused by them is principally inflicted on wood in direct contact with the ground.

In addition to termites, structural wood can be degraded by a plurality of insects, mostly beetle pests of which the most notorious ones are *Anobium punctatum*, *Lyctus brunneus* and *Hylotrypes bajulus*. Of these insects, *A. punctatum* is capable of degrading the sapwood of many species of coniferous and deciduous trees. *A. punctatum* utilizes the cellulosic component of wood and its gut contains yeasts and other microorganisms. While damage caused by *A. punctatum* is frequently associated with a high moisture content of the wood, in some cases insect attack has been found to occur at a moisture content as low as 15 %. *Hylotrypes bajulus* of the *Cerambycidae* family, which is common in Central and Southern Europe, is capable of degrading the sapwood of coniferous trees. *Lyctus brunneus* of the *Lyctidae* family known as a degrading infester of deciduous trees, is also a dangerous species causing great damage in Central and Southern Europe.

In addition to behaving as a fungicidal agent, a good wood preservative should be able to prevent damage from insects. Of wood preservatives currently in use, creosote oil, CCA and Na-PCP (pentachlorophenol) are also highly effective against insect attack. However, these wood preservatives have a wide toxic spectrum, and they contain a great number of components harmful to man and other nature. Consequently, the use of these preservatives is strictly controlled or even forbidden in many countries. Other compounds used for insect control are, e.g., solvent formulations of permethrin, dieldrin, bioresmethrin (pyrethroids), chloropyriphosphate and dichlorophosphate (organic phosphorus compounds) and some chlorinated hydrocarbons and carbamates. The use of these compounds also involves health and environmental risks.

According to current knowledge, boron compounds alone from the group of environmentally compatible compounds exhibit preservative properties against rot complemented with preservative efficacy against damage from insect attack (particularly from termites). However, boron is both expensive as a preservative and easily leached out from the wood.

Since a great number of insecticides used as wood preservatives are harmful to the environment, an urgent need exists to develop new preservation alternatives. Accordingly, it is an object of the present invention to overcome the drawbacks of prior-art technology and to provide an entirely novel approach to the preservation of wood from the attack of insects.

The goal of the invention is achieved by treating wood with an efficient amount of aminocarboxylate.

More specifically, the procedure according to the invention is characterized by what is stated in the characterizing part of claim 1.

As is generally known, metal-chelating agents such as aminocarboxylates are effective preservatives against wood decay caused by rot fungi. Their antirot effect is based on their capability of binding such metal species in the wood that are essential to the decay mechanism of rot fungi into a form making the metal species incapable of participating the fungal rot reactions. Hence, the preservative efficacy of these agents is not based on the general toxicity of aminocarboxylates, but instead on their specific inhibitory effect.

Unexpectedly, in conjunction with the present invention it has been found that aminocarboxylic acids and amino-

carboxylates also exhibit preservative efficacy against some insect species attacking wood. For the time being, the mechanism of the insecticidal efficacy in the present use remains unresolved. However, it is plausible that here these compounds work in a different role from that of a wood preservative, because transition metals contained in wood are not known to participate in the metabolism of insects, thus contributing to their breeding and infestation in wood.

The invention offers significant benefits. Hence, the suitability of aminocarboxylates as insecticides is enhanced by their water-solubility, nontoxic character and low cost. With the help of aminocarboxylates, both sawn timber (using soaking treatment) and plywood can be preserved, whereby in the latter application the insecticidal agent is added in the glue (glue line), or alternatively, the veneer sheets can be treated separately. Also the treatment of ready-bonded plywood is possible.

Since aminocarboxylic acids and aminocarboxylates can also preserve wood from damage caused by rot and staining fungi, the invention makes it possible to achieve comprehensive preservation of wooden products against both rot, staining and insect attack in a single treatment.

In the following, the invention will be examined in greater detail with the help of a detailed description and a number of examples.

In the context of the present invention, the term "wooden material" refers to both felled wood (e.g., logs), sawn lumber and worked wood (e.g., structural lumber). Wooden material must also be understood to include composite materials such as plywoods and particle boards. Both deciduous and coniferous wood may be used in the wooden material. Thus, the invention can be used for preserving coniferous wood products made from pine, spruce or larch, or deciduous wood products made from, e.g., oak, beech, ash, birch, alder, poplar or aspen.

The term "insecticide", or correspondingly, the term "insecticidal agent" in the present context is used in making reference to an agent capable of preventing the breeding and infestation of insects in a substrate in such a manner that the insects or their larvae cannot utilize a wooden material as their nutrient or nesting environment. Hence, an additional role of the insecticide is to prevent sudden degradation of the strength properties of a wooden material.

The procedure according to the invention is used in preservation of wood against damage from insects chiefly belonging to three orders: *Isoptera*, *Coleoptera* and *Hymenoptera*. Wood-degrading termites are those of the order *Isoptera*; particularly noteworthy of them are the *Coptotermes formosanus* and *Mastotermes darwiniensis* termite species. Other important insect species are *Anobium punctatum* (furniture beetle), *Lyctus brunneus* (powder-post beetle), and *Hylotrupes bajulus* (house longhorn).

A particularly high preservation efficacy is achieved against attack from termites of the *Coptotermes* family and house longhorn.

According to the invention, the insecticidal agent used is an aminopolycarboxylic acid or a salt thereof having, e.g., acetic acid as the acid component. Examples of suitable compounds are aminodi-, aminotri- and aminotetracarboxylates including ethylene-diaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), n-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediamine-di-(o-hydroxyphenylacetic acid (EDDHDA), diethanolglycine (DEG) and ethanololdiglycine (EDG), as well as alkali metal and earth alkali metal salts thereof including $\text{Na}_2\text{H}_2\text{EDTA}$ and Na_4EDTA .

According to the invention, wood is treated with an insecticidally effective amount of an aminocarboxylate or aminocarboxylic acid. Optimal preservative contents for prevention of insect attack are 20 - 60 kg/m³ of wood volume in sawn lumber and 10 - 15 kg/m³ of wood volume in plywood. The wooden material is impregnated most advantageously as deep as possible with a solution having aminocarboxylic acid or a salt thereof, or alternatively, a mixture of aminocarboxylic acids or salts thereof, as the preventive agent. The concentration of the active agent in the solution may be varied in a wide range. Typically, the active agent is used for about 0.01 - 50 %, advantageously about 0.1 - 30 %, of the solution weight. The amount used varies according to the moisture content and transition metal content of the wood. Typically, in pressure impregnation the consumption of the preservation solution is about 300 - 500 l per cubic meter of wood when the wood moisture content is 20 % and the concentration of the active agent in the solution is about 25 %. Hence, if the mass of the wood being treated is 1 kg and the averaged density of the wood is about 500 kg/m³, the amount of preservative solution consumed in the impregnation process is about 0.6 - 1.0 l.

The solvent of the solution is advantageously water and the wood preservative may also be complemented with other conventionally used additives which promote the penetration of the solution into the wood. In addition to the biologically inert additives, the wood preservative according to the invention can contain conventional biologically active agents such as boron compounds, copper ions or complex compounds of copper. Besides water, also other solvents (e.g., alcohols such as ethanol and methanol), or alternatively, mixtures of water and such solvents, may be used for dissolving the aminocarboxylic acids or carboxylates. Herein, the proportion of water in these mixtures may vary in the range 1 - 99 vol.-%. Also various kinds of emulsions may be contemplated, whereby the active insecticide and the possible additives are dissolved in solvents of different phases of the emulsion. Thus, the expression "the aminocarboxylic acid and/or the salt thereof is impregnated into the wood in a solution" covers both the first alternative procedure in which impregnation is performed using a solution or mixture in which the active agent is in dissolved form as well as the second alternative procedure in which impregnation is carried out using an emulsion in which the active agent

is not necessarily dissolved in all phases of the emulsion.

When desired, the aminocarboxylic acid or the aminocarboxylate can be precipitated into the wood, whereby a depot is formed serving to release the active agent so as to compensate for the leaching-out of the liquid-phase aminocarboxylic acid or aminocarboxylate from the wood. The precipitation of the active agent into the wood can be implemented at least in two different methods, namely through changing the pH or temperature of the solution. These methods are described more closely in FI Pat. No. 93,707.

The impregnation of the active insecticide preservative into the wood can be performed using any conventional technique including a pressure, a vacuum or a combination vacuum/pressure impregnation process. According to one alternative process, the aminocarboxylate solution is impregnated into the wooden material using a vacuum of about 10 - 95 %, advantageously about 70 - 90 %, of the atmospheric-air pressure (using a process time of about 10 min - 5 h, advantageously about 30 min - 2 h). Subsequently, the excess solution of the aminocarboxylic acid or the aminocarboxylate is removed, which step is first performed at atmospheric-air pressure and then in a partial vacuum. According to another alternative process, the method is carried out by impregnating said solution into the wood at an elevated temperature of, e.g., about 30 - 80 °C under pressure (about 2 - 6 barg, treatment time 5 min - 1 h). Subsequently, the pressure is elevated to 10 - 15 barg for 0.5 - 5 h in order to obtain improved penetration. After the impregnation step, the process pressure is reduced rapidly, the solution is dumped and the wood is subjected to posttreatment (in a vacuum of about 70 - 90 % of atmospheric-air pressure), wherein the evaporation of the penetrated solution results in the precipitation of the aminocarboxylic acid or the aminocarboxylate.

Furthermore, the solution of the aminocarboxylic acid or the aminocarboxylate and the acid solution can be alternatively penetrated into wood by means of soaking. This latter alternative process is easy to implement through, e.g., immersing the sawn lumber first in a vessel containing said active agent and then transferring the lumber after a desired time to another vessel filled with an acid solution. The soaking process is carried out using a maximally saturated solution, whereby the impregnation and acid treatment steps may vary in the range of about 1 min - 5 h. Typically, the soaking process of green sawn lumber is in the range of about 30 min - 2 h.

Next, the invention is elucidated with a number of examples. The exemplifying agent of the aminocarboxylate moiety in the examples is EDTA, whose efficacy on damage caused by insects was investigated by means of modified EN tests. The tests were carried out in Germany, in the facilities of BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin). The test measures the resistance of EDTA-preserved plywood or sawn lumber to damage caused by termites and house longhorn (*Hylotrupes bajulus*).

Example 1

The termite resistance of birch plywood having the sheets glued together using EDTA as the preservative in the glue (7 ply; 10 kg EDTA/m³) was tested according to the EN 117 standard using two termite species (*Coptotermes formosanus* and *Mastotermes darwiniensis*).

The *Mastotermes* termites degraded the comparative samples of plywood almost completely. While more material was left from test pieces containing EDTA, the efficacy of the preservative must be considered insufficient. By contrast, EDTA exhibited high efficacy as a preservative against damage from *Coptotermes* termites. In the *Coptotermes* termite test, all comparative samples were thoroughly bitten. Test pieces containing EDTA were weakly bitten with the exception of one test piece. Test pieces made from pine were destroyed fully. The EDTA-containing test pieces caused almost total eradication of termite workers with the exception of one test piece in which about one-third of the workers stayed alive. The results of the termite test are given in Table 1.

Table 1.

Efficacy of EDTA against damage caused by <i>Coptotermes formosanus</i> termites. Test pieces were subjected to attack by 200 workers and 30 soldiers. Test conditions were set to 26 °C and 92 %RH. Test duration was 39 days.				
Treatment	Sample no. in each batch	Living termites (%)		Notes
		Workers	Soldiers	
Comparative plywood sample	1	89	83	All test pieces thoroughly bitten
	2	94	83	
	3	90	97	
	4	94	87	

Table 1. (continued)

Efficacy of EDTA against damage caused by <i>Coptotermes formosanus</i> termites. Test pieces were subjected to attack by 200 workers and 30 soldiers. Test conditions were set to 26 °C and 92 %RH. Test duration was 39 days.				
Treatment	Sample no. in each batch	Living termites (%)		Notes
		Workers	Soldiers	
Test plywood containing EDTA in glue	1	0	0	Weakly bitten
	2	36	83	Thoroughly bitten
	3	4	30	Weakly bitten
	4	9	67	Weakly bitten
Comparative pine samples	1	92	73	All test pieces destroyed
	2	92	100	
	3	87	90	

Example 2

The house longhorn test (*Hylotrupes bajulus*) was performed according to the EN 47 standard. The pine sapwood test pieces were vacuum-impregnated with 10 % Na₂-EDTA or Na₄-EDTA solution. The impregnated test pieces and nonimpregnated comparative samples were subjected to attack by the larvae of *H. bajulus* so that into each test piece were drilled six holes, after which a larva was placed in each of the holes. At the end of the test, the test pieces were split and the number of surviving larvae was counted.

EDTA exhibited high efficacy against attack by the larvae of *H. bajulus*. In test pieces treated with Na₄-EDTA, all larvae died during four weeks. In test pieces treated with Na₂-EDTA, all larvae were found dead at the end of the 8-week test period. The test results are given in Table 2.

Table 2.

Efficacy of Na ₂ -EDTA and Na ₄ -EDTA against attack from the larvae of house longhorn (<i>Hylotrupes bajulus</i>).						
Treatment	Number of samples in batch	Test duration (weeks)	Total number of larvae (pcs.)			Larvae lost (pcs.)
			Dead		Surviving	
			no attack	attack	attack	
Compar. sample Na ₄ -EDTA	5	4	1	0	28	1
	5	4	1	29	0	0
Compar. sample Na ₂ -EDTA	5	12	0	0	29	1
	4	4	0	23	1	0
	1	12	0	6	0	0

The efficacy of EDTA against attack by furniture beetle (*Anobium punctatum*) has also been investigated, and these test results indicate at least a good efficacy.

Claims

- Use of an aminocarboxylic acid or aminocarboxylate for wood preservation against insect attack.
- Use as defined in claim 1, **characterized** in that said aminocarboxylic acid or aminocarboxylate is selected from the group of compounds comprising aminodi-, aminotri- and aminotetracarboxylic acids and carboxylates.

3. Use as defined in claim 2, **characterized** in that said group of compounds comprises ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), n-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediamine-di-(o-hydroxyphenylacetic acid (EDDHDA), diethanolglycine (DEG) and ethanoldiglycine (EDG), as well as alkali metal and earth alkali metal salts thereof.
4. Use as defined in claim 3, **characterized** in that said compound is $\text{Na}_2\text{H}_2\text{EDTA}$ or Na_4EDTA .
5. Use as defined in any of the foregoing claims, **characterized** in that wood is preserved against the attack of termites of the *Coptotermes* family or the house longhorn (*Hylotrupes bajulus*).
6. Use as defined in any of the foregoing claims, **characterized** in that in the preservation process is used 1 - 100 kg, advantageously about 5 - 80 kg aminocarboxylic acid or aminocarboxylate per cubic meter of wood.
7. Use as defined in any of the foregoing claims, **characterized** in that sawn lumber, plywood or particle board is preserved.
8. Use as defined in claim 6 or 7, **characterized** in that the preservative consumption in the preservation of sawn lumber is 20 - 60 kg/m^3 of wood volume, and in the preservation of plywood, 10 - 15 kg/m^3 of wood volume.
9. Use as defined in any of the claims 6 - 8, **characterized** in that the sawn lumber is vacuum-impregnated with EDTA or a potassium salt thereof.
10. Use as defined in any of the claims 6 - 8, **characterized** in that the EDTA or the potassium salt thereof is added to the glue of the plywood or particle board.
11. Use as defined in any of the foregoing claims, **characterized** in that an aqueous solution of the potassium salt of EDTA is used.
12. Use as defined in claim 11, **characterized** in that the potassium salt of EDTA is fixed in the wood by precipitation from said aqueous solution.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 66 0107

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO 93 08971 A (SUOMEN PUUTUTKIMUS OY) * the whole document *	1-12	B27K3/36 B27K3/34
A	WO 94 22647 A (KYMME OY ;KOSKISEN OY (FI) ; METSAELIITTO OSUUSKUNTA (FI); * the whole document *	1-12	
A	WO 94 22647 A (KYMME OY ;KOSKISEN OY (FI) ; METSAELIITTO OSUUSKUNTA (FI)) * the whole document *	1-12	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B27K

Place of search

THE HAGUE

Date of completion of the search

9 December 1997

Examiner

Dalkafouki, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another
document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or
after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding
document

EPO FORM 1503 03.82 (P4/C01)

(12) UK Patent Application (19) GB (11) 2 368 284 (13) A

(43) Date of A Publication 01.05.2002

(21) Application No 0118880.4

(22) Date of Filing 03.08.2001

(30) Priority Data

(31) PQ9173

(32) 04.08.2000

(33) AU

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(51) INT CL⁷

A01N 37/44 55/02

(52) UK CL (Edition T)

A5E EAB E228 E239 E247 E274 E277 E279

U1S S1290

(56) Documents Cited

GB 2339694 A

WO 97/26789 A1

US 3442922 A

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WO 96/05728 A1

(58) Field of Search

Online: CAS ONLINE

(54) Abstract Title

Compositions comprising metal salts or complexes of ethylenediamine tetraacetic acid (EDTA) for controlling terrestrial molluscs

(57) Compositions are provided for the control of terrestrial molluscs which are capable of acting as an effective, readily ingestable poison that is lethal to terrestrial molluscs, the composition including as an active component a metal salt or complex of edetic acid (also known as ethylene diamine tetra-acetic acid (EDTA)). The metal is preferably chosen from Group IB (Group 11) of the Periodic Table, especially copper. Preferred active ingredients are Cu-EDTA and Cu₂-EDTA complexes.

The compositions may comprise a carrier selected from agar, dextrose agar, gelatine, oil cake, pet food, cereal, fruits, fish by-products, sugars, malt vegetable matter (eg cereal grains), casein, blood meal, bone meal, yeast, fats, paper, mineral substrates and colorant. The compositions may include additional formulation enhancing additives, such as preservatives or anti-microbial agents, phagostimulants, waterproofing agents, and taste altering additives, (eg bittersweetening denatonium benzoate).

The constituents of the composition are relatively environmentally safe and pose very low threat to humans, animals (eg pets) or other non-pests.

GB 2 368 284 A

Compositions and Methods for controlling molluscs

Field of the invention

The present invention relates to compositions for the control of terrestrial molluscs. More particularly the invention relates to an effective, readily ingestable poison that is lethal to terrestrial molluscs.

Background of the invention

In this specification, where a document, act or item of knowledge is referred to or discussed, this reference or discussion is not an admission that the document, act or item of knowledge or any combination thereof was at the priority date, publicly available, known to the public, part of the common general knowledge or known to be relevant to an attempt to solve any problem with which this specification is concerned.

In this specification, references to edetic acid, also known as ethylene diamine tetra-acetic acid, are often as a shorthand abbreviated to "EDTA".

Accordingly in this specification a reference to EDTA is a reference to edetic acid. Furthermore, a reference to a complex of EDTA includes complex salts and coordination compounds of EDTA.

Terrestrial pulmonate gastropods, slugs and snails (collectively, molluscs) are significant plant pests that affect commercial agriculture, horticulture and domestic gardens. These molluscs are omnivorous and consume large amounts of vegetative materials during their daily foraging. Consequently, they can seriously damage vegetable gardens and plant crops during all phases of the growth cycle. Because of the destructive potential of terrestrial molluscs, control measures must be employed to ensure adequate protection of the growing plants.

A wide variety of approaches have been used to try to combat mollusc pests. Perhaps the most common is the use of poisonous actives called molluscicides. Molluscicides include a diversity of chemical compounds such as table salt (NaCl), calcium arsenate, copper sulfate, mesurol and metaldehyde. Molluscicides fall into two major categories based on their mode of action – (1) contact poisons, and (2) baits, which include ingestible poisons.

Contact poisons are molluscicides that must come into physical contact with the exterior of the mollusc in order to be effective. Physical contact usually occurs either by external

application or through the action of the mollusc traversing a molluscicidal composition placed on the ground. The contact molluscicide is picked up by the proteinaceous slime coat of the mollusc and it builds up in the body of the mollusc until a lethal level is reached.

5 One of the major drawbacks of contact molluscicides is that they have little effect if the molluscs do not have sufficient physical contact with the chemical agents. If the molluscs are hidden or migrate into an area after a contact molluscicide is spread, they are unaffected. For these reasons, contact-acting mollusc poisons are generally considered to be unreliable.

10 Mollusc baits must be ingested by a mollusc in order to be lethal. Baits tend to be preferred over contact poisons because baits are considered more reliable.

One challenge associated with the development of effective mollusc bait is preparation of a composition that is both palatable to the mollusc and is effective in delivering a lethal poison. Obviously, a sufficient quantity of the poison must be ingested to reach the lethal
15 threshold. Often, compositions that are palatable to the mollusc are not effective as a lethal poison, while compositions that are quite potent and lethal are often not readily ingested by molluscs or are repellents.

Many contact poisons, such as aluminium sulfate, copper sulfate and borax, are useless as ingestible poisons for baits because they are so unpalatable, the molluscs will not ingest a
20 lethal dose. Baits must be sufficiently palatable that a mollusc will build up the dose of poison in its system, but the poison must also be slow acting enough to prevent the mollusc from becoming sick or cause it to cease feeding.

Typical problems associated with the development of compositions for the effective control of molluscs are discussed by Henderson, et al in Aspects of Appl. Biol. (1986) 13,
25 341-347. This publication recognises that although many compounds are known to be poisonous to molluscs, there is considerable difficulty in delivering the poison to the mollusc either as bait or as a contact poison. The potential toxicity of a compound is irrelevant if molluscs will not consume a lethal dose of a bait poison.

One of the few compounds that can be used as either a contact or bait poison for terrestrial
30 molluscs is metaldehyde. This compound is commonly used as a long lasting bait, attracting molluscs and killing them after ingestion. While metaldehyde has high

effectiveness and commercial popularity, it has the serious drawback of being toxic to higher mammals and is a major contributor to domestic animal poisoning in the United States, Europe and Australia.

Therefore there is need to develop an effective ingestible poison for molluscs that is
5 palatable to molluscs yet does not pose a threat to the environment, crops, animals and other non-pests.

Accordingly, it is an object of the invention to provide a composition and method for killing terrestrial molluscs that is palatable to the molluscs and overcomes one or more of the problems associated with the baits of the prior art.

10 **Summary of the invention**

The invention provides in one embodiment a composition for the control of terrestrial molluscs, the composition comprising as an active ingredient at least one metal salt of EDTA or metal EDTA complex.

The present invention provides in another embodiment an ingestible composition for the
15 control of terrestrial molluscs, the composition being as described herein.

The present invention provides in another separate embodiment a molluscicidal bait including a composition as described herein.

The present invention provides in another embodiment a method for controlling terrestrial molluscs, the method comprising the step of exposing the mollusc to a composition as
20 described herein.

The present invention provides in another embodiment a method for controlling terrestrial molluscs, the method comprising the step of applying to a substrate a composition as described herein, and exposing the substrate to the mollusc.

The present invention provides in another embodiment a method for controlling terrestrial molluscs, the method comprising the step of applying to a substrate an ingestible
25 composition, the composition being as described herein, and exposing the substrate to the mollusc.

The present invention provides in another embodiment a method for controlling terrestrial molluscs, the method comprising the step of applying to an area to be controlled a
30 composition as described herein.

The metal may be any suitable metal capable of forming a salt or a complex with edetic acid. The metal is preferably a Group IB element of the Periodic Table. Most preferably the metal is copper. Other metals are envisaged within the scope of the present invention.

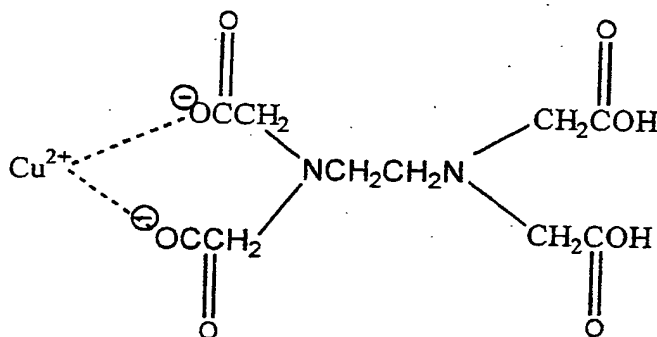
The carrier may take any suitable form. The carrier will typically be an inert carrier,
5 preferably an inert carrier that is readily consumed by molluscs. A variety of suitable inert carriers are well known and may be used in the compositions of the present invention.

Such inert components include, non-exhaustively, agar, dextrose agar, gelatine, oil cake, pet food, cereal, fruits, fish by-products, sugars, malt, vegetable matter, casein, blood meal, bone meal, yeast, fats, paper and colorant. The preferred inert component is wheat cereal
10 which is readily commercially available from various sources.

The composition in a preferred embodiment combines an inert carrier with a copper EDTA complex. When copper is the metal selected for formation of a metal complex with EDTA, the copper EDTA complex is preferably present in the composition an amount such that the concentration of copper within the composition is in the range of about 10 to
15 200,000 ppm, more preferably 17 to 27,000 ppm. More preferably, the copper EDTA complex should be present in an amount such that the copper concentration in the composition is in the range of about 2,500 to 10,500 ppm.

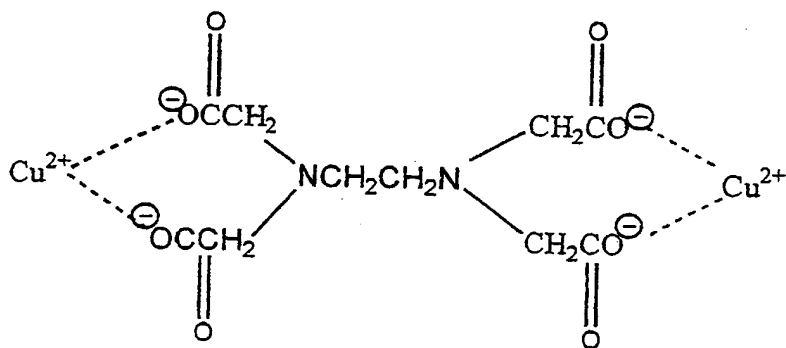
Suitable copper EDTA complexes for use in the composition of the present invention will be readily apparent to the skilled addressee. In a preferred embodiment the copper EDTA
20 complex is Cu-EDTA and/or Cu₂-EDTA as depicted below.

Cu-EDTA



($\text{Cu C}_{10} \text{H}_{14} \text{N}_2 \text{O}_8$ $M_r = 353.7702$)

and/or

 Cu_2 -EDTA

($\text{Cu C}_{10} \text{H}_{12} \text{N}_2 \text{O}_8$ $M_r = 415.3004$)

The substrate according to the invention may take any suitable form. It will typically be a foodstuff normally consumed by a terrestrial mollusc, such as a plant leaf or a seed, such as vegetable or cereal seeds. It may be a mineral substrate, such as dolomite chips. Other substrates are envisaged within the scope of the present invention.

- 5 The composition will typically be applied to the substrate, thereby exposing the mollusc to the composition. The composition may be applied to the substrate such as by coating. In an alternative embodiment the composition and the substrate may be combined as an intimate mixture.

- 10 On exposure to the composition, typically by consuming at least part of the substrate to which the composition has been applied, it is believed that the composition becomes toxic to the mollusc after ingestion.

- One advantage of the compositions of the present invention is that they exhibit good mortality against terrestrial molluscs and is readily consumed by terrestrial molluscs. A further advantage of this composition is that the constituents of the composition are
15 relatively environmentally safe and pose very low threat to humans, animals or other non-pests.

Compositions according to the invention may include additional formulation enhancing additives. Such additives include preservatives or anti-microbial agents, phagostimulants, waterproofing agents, and taste altering additives.

- 20 A variety of preservatives can be used effectively with this molluscicidal bait composition. Preservatives can normally be mixed with water to form a stock solution which would typically be added to the formulation at a concentration in the range of about 10-50,000 ppm.

- One or more phagostimulants can be added to the composition to attract molluscs and to
25 induce molluscs to feed upon the composition. A variety of phagostimulants can be used, including sugars, malt, yeast products and casein. Sugars, such as sucrose, are among the more preferred phagostimulants. These additives are normally incorporated within the composition in a dry form. Typically, they can be added to the composition at about 1 to 2.5% by weight of the total composition.

- 30 Waterproofing agents, that can also act as binders, can be added to the composition to improve the weatherability of the molluscicidal bait. These are typically water insoluble

compounds such as waxy materials and other hydrocarbons. Examples of suitable waterproofing agents are paraffin wax, stearate salts, beeswax, and similar compounds. Waterproofing agents can be incorporated into the composition, in dry form, typically at a concentration of about 5 to 12% by weight of the total composition.

- 5 It is also possible to include in the molluscicidal bait taste altering compounds that render the composition unpalatable to higher animals. Suitable taste altering compounds include those having a bitter taste. Suitable commercially available taste altering compounds include denatonium benzoate. These compounds typically are added at very low concentrations.
- 10 The molluscicidal bait of this invention is typically used in dry form and many of the constituent ingredients of the composition are included in dry form. However, it is useful to include an amount of water within the composition which is sufficient to form a damp pre-mix so that the ingredients can be more easily formed. Water is typically added at about 5 to 90% by weight of the total composition.
- 15 As noted above, the bait of the present invention can be used in any convenient form and is typically used as a powder, granules, cubes, pellets, sprays or gels. The composition may be spread on or around areas infested by molluscs as well as in areas in which it is desirable to prevent mollusc infestation.

- The present invention also provides a method of preparing a mollusc bait comprising the
- 20 steps of blending the active component with one or more inert components and any optional additives. For example, mollusc baits according to the present invention can be prepared as follows: a suitable amount of the active ingredient is blended, in dry form, with a dry inert component such as wheat flour. Thereafter, optional additives (such as phagostimulants and waterproofing agents) are blended and mixed with the other
- 25 components. Next, suitable amounts of liquid optional additives (such as preservatives, taste altering components and water) are added to the dry mixture to form a damp pre-mix. The pre-mix can then be made into a desired form, such as a powder, granules, cubes, pellets, spray or gel.

- Alternatively, the bait of the present invention may be prepared by coating a suitable inert
- 30 component with at least one EDTA complex. Typically the inert component is vegetable matter, cereal or mineral matter. It is particularly preferred that the coated inert component is vegetable seed or cereal grain or dolomite.

EXAMPLE 1

Molluscicidal baits were prepared according to the general procedure discussed above. The active ingredient precursors were added in sufficient amounts to yield the different concentrations of copper (present as copper EDTA) in the bait (see Table 1):

5 Table 1: Active concentrations in trial baits.

Bait Identifier	Copper Concentration
T1	2,500 ppm
T2	5,000 ppm
T3	7,500 ppm
T4	10,000 ppm
Control	0 ppm

The control was prepared in a similar manner, except that it did not include the active ingredient copper EDTA.

10 Tests were conducted in 30cm x 45cm x 5cm plastic containers. Duplicate tests were carried out for each of the different bait active concentrations with common garden snails (*helix aspersa*), Italian white snail (*theba pisana*) and slugs (*deroceras reticulatum*). Each trial had 10 snails or slugs introduced to the trial containers (see Table 2, Table 3 and Table 4):

Table 2: Description of the different trials with *helix aspersa*.

Trial Identifier	Copper Concentration
T1 HA1	2,500 ppm
T1 HA2	2,500 ppm
T2 HA1	5,000 ppm
T2 HA2	5,000 ppm
T3 HA1	7,500 ppm

Trial Identifier	Copper Concentration
T3 HA2	7,500 ppm
T4 HA1	10,000 ppm
T4 HA2	10,000 ppm
Control HA1	0 ppm
Control HA2	0 ppm

Table 3: Description of the different trials with *theba pisana*.

Trial Identifier	Copper Concentration
T1 W1	2,500 ppm
T1 W2	2,500 ppm
T2 W1	5,000 ppm
T2 W2	5,000 ppm
T3 W1	7,500 ppm
T3 W2	7,500 ppm
T4 W1	10,000 ppm
T4 W2	10,000 ppm
C W1	0 ppm
C W2	0 ppm

Table 4: Description of the different trials with *deroceras reticulatum*.

Trial Identifier	Copper Concentration
T1 S1	2,500 ppm

Trial Identifier	Copper Concentration
T1 S2	2,500 ppm
T2 S1	5,000 ppm
T2 S2	5,000 ppm
T3 S1	7,500 ppm
T3 S2	7,500 ppm
T4 S1	10,000 ppm
T4 S2	10,000 ppm
Control S1	0 ppm
C S2	0 ppm

Each tray was floored with damp potting soil and covered with a transparent, plastic lid with air holes. Ten grams of the formulations identified above in Table 1 were placed inside a petrie dish and put in each plastic tray along with a lettuce plant. The plastic containers were placed outside in the shade during the course of the experiment.

- 5 The following observations were made 4 days after the snails and slugs were placed in the trial containers.

Trial	Number of Dead Molluscs	Mass of Pellet Consumed (g)	Lettuce Plant Consumed (%)
T1 HA1	6	4.6	10
T1 HA2	5	5.1	5
T2 HA1	8	4.5	10
T2 HA2	9	3.9	0
T3 HA1	10	3.8	0
T3 HA2	10	4.0	5
T4 HA1	10	2.5	0

Trial	Number of Dead Molluscs	Mass of Pellet Consumed (g)	Lettuce Plant Consumed (%)
T4 HA2	10	3.0	5
Control HA1	0	Not Applicable	95
Control HA2	0	Not Applicable	95
T1 W1	7	4.9	15
T1 W2	7	4.6	30
T2 W1	8	3.2	5
T2 W2	9	4.1	5
T3 W1	10	4.4	0
T3 W2	10	5.0	0
T4 W1	10	3.5	0
T4 W2	10	3.1	0
Control W1	0	Not Applicable	100
Control W2	0	Not Applicable	95
T1 S1	5	7.4	15
T1 S2	6	5.3	10
T2 S1	9	6.1	5
T2 S2	8	6.5	5
T3 S1	10	7.3	0
T3 S2	10	5.6	5
T4 S1	10	4.7	0
T4 S2	10	4.2	0
Control S1	1	Not Applicable	95
Control S2	0	Not Applicable	100

Pellets manufactured with 7,500 ppm and 10,000 ppm achieved a 100% kill rate. The lower concentrations although effective (a 100% kill rate was observed on day 8 for the 2,500 ppm and 5,000 ppm products) the snail and/or slugs were able to cause significant damage to the lettuce plant.

- 5 The word 'comprising' or forms of the word 'comprising' as used in this description does not limit the invention claimed to exclude any variants or additions.

Whilst it has been convenient to describe the invention herein in relation to particularly preferred embodiments, it is to be appreciated that other constructions and arrangements are considered as falling within the scope of the invention. Various modifications, alterations,
10 variations and or additions to the constructions and arrangements described herein are also considered as falling within the scope and ambit of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composition for the control of terrestrial molluscs, the composition comprising as an active ingredient at least one metal salt of EDTA or metal EDTA complex.
2. A composition according to claim 1 wherein the metal is chosen from Group IB of the Periodic Table.
3. A composition according to claim 2, wherein the metal is copper.
4. A composition according to claim 1 wherein the metal EDTA complex is a copper EDTA complex.
5. A composition according to claim 4, wherein the copper EDTA complex is Cu-EDTA and/or Cu₂-EDTA as herein defined.
6. A composition according to any one of the preceding claims, wherein said composition is in the form of an ingestible bait.
7. A composition according to any one of the preceding claims, which further includes a carrier.
8. A composition according to claim 7, wherein said carrier is inert.
9. A composition according to claim 7 or 8, wherein said carrier is selected from agar, dextrose, agar, gelatine, oil cake, pet food, cereal, fruits, fish by-products, sugars, malt, vegetable matter, casein, blood meal, bone meal, yeast, fats, paper, colorant(s), mineral substrates and mixtures thereof.
10. A composition according to any one of the preceding claims, and further including one or more formulation enhancing additives.
11. A composition according to claim 10, wherein said formulation enhancing additive is chosen from preservatives, anti-microbial agents, phagostimulants, waterproofing agents, taste altering additives and combinations of one or more of these.
12. A composition according to any one of the preceding claims, wherein said composition is provided in dry form.
13. A composition according to any one of claims 1 to 12, wherein said composition is provided in liquid form.

14. A composition according to any one of the preceding claims which is in a form chosen from the group consisting of powders, granules, cubes, pellets, sprays or gels.
15. A composition according to any one of the preceding claims, wherein the concentration of metal in said composition is in the range of from 10 to 200,000 ppm.
16. A composition according to any one of the preceding claims, wherein the concentration of metal in the composition is in the range of from 17 to 27,000 ppm.
17. A composition according to any one of the preceding claims, wherein the concentration of metal in said composition is in the range of from 2,500 and 10,000 ppm.
18. A composition according to claim 10 or 11, wherein said additive is a preservative present in said composition at a concentration in the range of from 10 to 50,000 ppm.
19. A composition according to claim 10, wherein said additive is a phagostimulant present in said composition at a concentration in the range of from 1 to 2.5% by weight of the composition.
20. A composition according to claim 10, wherein said additive is a waterproofing agent present in said composition at a concentration in the range of from 5 to 12% by weight of the composition.
21. A composition for the control of terrestrial molluscs, substantially as hereinbefore described and with reference to the Example.
22. A molluscicidal bait including a composition as claimed in any preceding claim.
23. A method for controlling terrestrial molluscs comprising the step of exposing the mollusc to a composition as claimed in any one of claims 1 to 22.
24. A method for controlling terrestrial molluscs comprising the step of applying to a substrate a composition as claimed in any one of claims 1 to 22, and exposing the substrate to a terrestrial mollusc.
25. A method according to claim 24, wherein said substrate is a foodstuff normally consumed by a terrestrial mollusc.

26. A method for controlling terrestrial molluscs, the method comprising the step of applying to an area to be controlled, a composition as claimed in any one of claims 1 to 22.
27. A method for controlling terrestrial molluscs, substantially as hereinbefore described and with reference to the Example.
28. A method for preparing a terrestrial mollusc bait including the composition of claim any one of claims 1 to 22, the method comprising the steps of;
- (a) blending together the dry components of the bait to form a dry mix,
 - (b) adding liquid components to the dry mix to form a pre-mix, and
 - (c) making the pre-mix into the preferred form.
29. A method for preparing a terrestrial mollusc bait including the composition of any one of claims 1 to 22 comprising the step of coating vegetable material, cereal or mineral substrate with said composition.
30. A method according to claim 29, wherein vegetable seeds are coated with said composition.
31. A method according to claim 29, wherein cereal grains are coated with said composition.
32. A method according to claim 29, wherein dolomite is coated with said composition.
33. A molluscicidal bait, substantially as hereinbefore described and with reference to the Example.



INVESTOR IN PEOPLE

Application No: GB 0118880.4
Claims searched: 1-33

Examiner: Stephen Quick
Date of search: 18 February 2002

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T):

Int Cl (Ed.7):

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2339694 A (C L YOUNG), see pages 10 (lines 6-7 & 16-22) & 11 (formulations F1, F2, PSO, Phy10, Zn & Cu)	1-4, 6-9, 12, 14, 15 & 22 at least
X	GB 0715976 A (F C BERSWORTH), see (for example) pages 1 (lines 55-63), 2 (lines 28-61 & 99-112) & 3 (lines 33-42 & 45-48)	1, 6-9, 12-14 & 22 at least
X	WO 97/26789 A1 (C L YOUNG), see whole document, especially pages 1 (lines 5-7), 6 (lines 13-23), 8 (lines 9-10, 19-22 & 36-end), 9 (lines 1-12), 10 (lines 17-18), 11 (line 8), 12 (lines 1-15), 14 (example 1) & 16 (lines 27-28)	1-12, 14-20, 22-26 & 28-31
X	WO 96/05728 A1 (W NEUDORFF), see whole document, especially pages 2 (lines 35-37), 6 (lines 28-39), 7 (lines 1-4), 14 (lines 5-10), 15 (table 6A, formulation 6E), 16 (lines 16-21) & 17 (table 8A, formulations 8A, 8B & 8D)	1, 19, 20, 23, 25, 28 & 29 at least
X	US 3442922 A (DOW CHEMICAL), see the saturated solution at column 5 lines 32-42	1, 13 & 14

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



INVESTOR IN PEOPLE

Application No: GB 0118880.4
Claims searched: 1-33

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Date of search: 18 February 2002

Category	Identity of document and relevant passage	Relevant to claims

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 25/00, 37/44, C05G 3/02	A1	(11) International Publication Number: WO 99/39576 (43) International Publication Date: 12 August 1999 (12.08.99)
(21) International Application Number: PCT/EP99/00740 (22) International Filing Date: 4 February 1999 (04.02.99) (30) Priority Data: 60/073,827 5 February 1998 (05.02.98) US (71) Applicant: W. NEUDORFF GMBH KG [DE/DE]; An der Mühle 3, D-31860 Emmerthal (DE). (72) Inventor: PURITCH, George, S.; 8120 Thompson Place, Saanichton, British Columbia V8Z 4V5 (CA). (74) Agent: COHAUSZ & FLORACK; Kanzlerstrasse 8a, D-40472 Düsseldorf (DE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ENHANCEMENT OF METAL MOLLUSCICIDES BY ETHYLENE DIAMINE DISUCCINIC ACID (57) Abstract An ingestible mollusc poison contains a simple metal compound, an activity enhancing additive such as ethylene diamine disuccinic acid (EDDS) and derivatives thereof, and a carrier material edible to molluscs. In one embodiment the active agent of the mollusc poison may be in the form of a metal complex of EDDS. The composition may be used alone or in conjunction with molluscicidal co-active agents and/or fertilizers.		

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5
ENHANCEMENT OF METAL MOLLUSCICIDES BY ETHYLENE DIAMINE DISUCCINIC ACID10
STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

Not applicable.

FIELD OF THE INVENTION

15

This invention relates to pest control compounds and, more particularly, to compositions effective to control pest molluscs by enhancing the effectiveness of metal poison absorption in molluscs.

20
BACKGROUND OF THE INVENTION25

Terrestrial pulmonate gastropods such as slugs and snails are significant plant pests that affect commercial agriculture and horticulture and domestic gardens. These organisms are omnivorous and consume large amounts of vegetative material during their daily foraging. Consequently, they can seriously damage vegetable gardens and even plant crops during all phases of the growing cycle. Because of their destructive potential, control measures must be used to ensure adequate protection of the growing plants.

30

Aquatic molluscs, including the fresh water snails *Bulinsu* sp., *Bulinus*, *Biomphalaria*, and *Oncomeania*, and vectors of parasitic worms (e.g., *Schistosoma*), are also pests. Aquatic molluscs are controlled by a number of synthetic and botanical compounds.

Terrestrial pulmonate gastropods and aquatic molluscs are collectively referred to herein as "molluscs."

5 A wide variety of approaches have been used to combat pest molluscs. Perhaps the most common is the use of poisonous compounds called molluscicides. Molluscicides encompass a diverse group of chemical compounds including table salt (NaCl), calcium arsenate, copper sulfate and metaldehyde. Molluscicides, depending upon their mode of action, fall into two major groups: (1) contact poisons or (2) ingested poisons. As a contact poison, the molluscicides must come into physical contact with the exterior of the mollusc, 10 either by external application or as a result of the mollusc traversing the bait on the ground. The poison is picked up by the proteinaceous slime coat of the mollusc and builds up in the mollusc's body until it reaches lethal proportions. One of the major drawbacks of contact -type molluscicides is that they have little effect if the molluscs are not physically touched by the chemical. Slugs or snails will be unaffected if they are hidden or migrate into an area 15 after application of a contact molluscicide.

One of the few compounds that acts as both a contact and ingested poison is metaldehyde. This compound is commonly used as a long lasting bait, attracting the molluscs and killing them after ingestion of the compound. Despite its high effectiveness 20 and its commercial popularity, metaldehyde is toxic to higher mammals and is a major contributor to domestic animal poisoning in the U.S. and Europe.

Heavy metals, including zinc, aluminum, copper and iron are all toxic to molluscs and are known to be effective molluscicides when used as contact poisons in the form of salts or chelates (Henderson, et al. 1990). Few of them, however, have been successful 25 commercially, perhaps because many such compounds are not palatable to molluscs and are not ingested in sufficient quantities to be effective. More recently, Henderson et al. (UK Patent Application 2 207 866A, 1988) discovered that specific complexes of aluminum with pentanedione compounds and iron with nitroso compounds would act both 30 as ingested and contact poisons.

U.S. Patent No. 5,437,870 (Puritch et al) discloses an ingestible mollusc poison having a carrier (e.g., a bait), a simple iron compound and a second component. The second component can be ethylene diamine tetracetic acid (EDTA), salts of EDTA, hydroxyethylene triamine diacetic acid, (HEDTA) or salts of HEDTA. Australian Patent Application No. 77420/98 also discloses a stomach-action molluscicide that includes a metal complexone (i.e., iron EDTA) and a carrier.

With the metal-based ingested poisons, the slug must eat and absorb the poison in large enough amounts to reach a lethal threshold. These compounds are much more difficult to formulate and use than are contact poisons, because the compounds are not always palatable to the slug. To be effective, these compounds must be ingested and digested within the mollusc digestive tract in sufficiently high levels to cause a pesticidal effect. However, the activity of such molluscicides must be slow enough acting to prevent the slug from prematurely becoming sick and to cease feeding on the poison before a lethal dose is ingested. (Henderson and Parker, 1986.) Many of the contact poisons (e.g., aluminum sulfate, copper sulfate, borax, etc.) are useless as ingested poisons because of their deterrence to slugs.

It would thus be desirable to provide a composition that will enhance absorption of stomach-action mollusc poisons without deterring ingestion of the poison by molluscs.

SUMMARY OF THE INVENTION

The invention provides a mollusc stomach poison composition that comprises a simple metal compound, an additive that enhances the activity and absorption of the metal, and a carrier material that is edible to molluscs. The composition is effective to kill molluscs upon being ingested by the mollusc.

The simple metal compound may include metals selected from the group consisting of iron, copper, zinc, aluminum, and mixtures thereof. The term "iron" as used herein is understood to refer to both the ferric and ferrous forms of iron. The activity enhancing

additive is a compound selected from the group consisting of ethylene diamine disuccinic acid, isomers of ethylene diamine disuccinic acid, salts of ethylene diamine disuccinic acid, metal complexes of ethylene diamine disuccinic acid and mixtures thereof. The carrier material is one that is edible to molluscs, and it preferably is a mollusc food.

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In another embodiment the composition comprises a metal complex of ethylene diamine disuccinic acid or isomers thereof. Metals from which the complex can be formed include iron, copper, zinc, and aluminum.

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In another embodiment the mollusc poison composition may also include a co-active ingredient, such as metaldehyde. In yet another embodiment the composition may include or be used with a fertilizer compound, such as a granular fertilizer.

As used herein, the term "mollusc" refers to both terrestrial and aquatic molluscs.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a composition that is an ingestible mollusc poison. In one embodiment, the composition includes a simple metal compound, an activity-enhancing additive which is believed to increase the efficacy of the metal compound, and a carrier that is edible to molluscs. Additional formulation enhancing additives may be included as well. Examples of such compounds include pH-adjusting compounds, preservatives, anti-microbial agents, phagostimulants, and taste-altering additives.

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The simple metal compound can be one that includes metals such as iron, copper, zinc, aluminum or mixtures thereof. Such a compound may be reduced elemental iron, metal proteins (e.g., iron proteins, copper proteins, zinc proteins, aluminum proteins), metal salts (e.g., iron salts, copper salts, zinc salts, aluminum salts and mixtures thereof), metal carbohydrates (e.g., iron carbohydrates, copper carbohydrates, zinc carbohydrates, aluminum carbohydrates and mixtures thereof). Specific examples of such compounds include iron acetate, iron chloride, iron phosphate, iron phosphate/sodium citrate

mixture, sodium iron phosphate, iron pyrophosphate, iron nitrate, iron ammonium sulfate, iron albuminate, iron sulfate, iron sulfide, iron choline citrate, iron glycerol phosphate, iron citrate, iron ammonium citrate, iron fumarate, iron gluconate, iron lactate, iron saccharate, iron fructate, iron dextrate, iron succinate, iron tartrate, copper acetate, copper chloride, copper phosphate, copper pyrophosphate, copper nitrate, copper ammonium sulfate, copper albuminate, copper sulfate, copper gluconate, copper lactate, copper saccharate, copper fructate, copper dextrate, zinc acetate, zinc chloride, zinc phosphate, zinc pyrophosphate, zinc nitrate, zinc ammonium sulfate, zinc albuminate, zinc sulfate, zinc gluconate, zinc lactate, zinc saccharate, zinc fructate, zinc dextrate, aluminum acetate, aluminum chloride, aluminum phosphate, aluminum pyrophosphate, aluminum nitrate, aluminum ammonium sulfate, aluminum albuminate, aluminum sulfate, aluminum gluconate, aluminum lactate, aluminum saccharate, aluminum fructate, and aluminum dextrate. It is understood that the term "iron" as used herein refers to both the ferric and ferrous forms of this element.

As noted above, the activity enhancing additive is one that improves the efficacy of the metal compound by enhancing the digestive absorption of the metal. A preferred activity enhancing additive is ethylene diamine disuccinic acid (EDDS), in both its naturally occurring and synthetic forms. Further, the activity enhancing additive may be in the form of isomers of ethylene diamine disuccinic acid, salts of ethylene diamine disuccinic acid, metal complexes of ethylene diamine disuccinic acid and mixtures thereof.

Activity enhancing additives such as EDDS, its isomers, and its derivatives, are believed to contribute to the rapid absorption of the simple metal compound from the mollusc digestive tract into the internal organs of the animal. This results in rapid, irreversible destruction of the cellular integrity of the mollusc which prevents continuing feeding on plant material, eventually leading to death. EDDS is believed to affect parts of the mollusc digestive system by allowing the metal to be more freely and quickly dispersed throughout the mollusc body. The result of such overload of metal results in pathological distress to the mollusc system.

EDDS is a hexadentate ligand that occurs naturally and which is produced by a number of microorganisms including the actinomycete, *Amycolatopsis japonicum* sp. nov. (Nishikori et al. J. Antibiot. 37:426-427 (1994); Goodfellow et al, *Systematics and Applied Microbiology* 20:78-84 (1997). The molecular formula for this compound is $C_{10}H_{16}N_2O_2$ for the acid and $C_{10}H_{13}N_2O_8Na_3$ for the trisodium salt. The acid has a molecular mass of 292.25 while the trisodium salt is 358.19. The compound can occur in three stereoisomers, [R,R], [R,S/S,R], and [S,S]. EDDS can also be synthesized by a reaction of L-aspartic acid and 1,2-dihaloethane, as disclosed in U.S. Patent No. 5,554,791.

EDDS has been developed commercially as a trisodium salt compound sold under the trademark Octaquest® E-30 by the Associated Octel Company Ltd. This compound has the ability to complex with metals to serve as a chelator. It has the advantage of easily biodegrading and does not persist in the environment (Schowanek et al., *Chemosphere* 34:2375-2391 (1997)). Hence, it has been proposed for use as a surfactant in laundry detergents as disclosed in U.S. Patent No. 4,704,233.

Useful salts of ethylene diamine disuccinic acid that may serve as an activity enhancing additive according to the present invention include alkali metal salts, alkali earth salts, ammonium salts and substituted ammonium salts of this compound, as well as mixtures thereof. Preferred salts include the sodium, potassium, and ammonium salts.

The activity enhancing additive may also be in the form of metal complexes of ethylene diamine disuccinic acid. Examples of such complexes include iron EDDS complexes, as well as copper, zinc, and aluminum complexes of EDDS. In one embodiment, the composition may be used without a simple metal compound as a separate component. Instead, the compound can be used in the form of a metal complex of EDDS, with metals selected from iron, copper, zinc, and aluminum.

Suitable carrier materials are those that are edible to molluscs. Mollusc foods are an example of a preferred type of carrier material. Examples of suitable mollusc food carriers include wheat flour, wheat cereal, agar, gelatin, oil cake, pet food wheat, soya,

oats, corn, citrus mash, rice, fruits, fish by-products, sugars, coated vegetable seeds, coated cereal seeds, casein, blood meal, bone meal, yeast, fats, beer products, and mixtures thereof. Examples of particularly useful mollusc foods include a bone meal - wheat flour mixture having a ratio of bone meal to wheat flour in the range of 50:50 to 90:10 and one formed from wheat flour and sugar at a ratio of wheat flour to sugar in the range of about 90:10 to 95:5.

Other compounds, as noted above, may be added to the composition as formulation enhancing additives. Such compounds include preservatives or antimicrobial agents, phagostimulants, waterproofing agents, taste altering additives, and pH-adjusting additives.

Exemplary preservatives include Legend MK[®], available from Rohm & Hass Company of Philadelphia, Pennsylvania, and CA-24, available from Dr. Lehmann and Co. of Memmingen/Allgäu, Germany. Preservatives such as these can normally be mixed with water to form a stock solution to be added to the formulation at a concentration in the range of about 10-750 ppm.

Phagostimulants can be added to the composition to attract molluscs and to induce molluscs to feed upon the composition. A variety of phagostimulants can be used, including sugars, yeast products, and casein. Sugars, such as sucrose, are among the more preferred phagostimulants. These additives are normally incorporated within the composition in a dry form. Typically, they can be added to the composition at about 1 to 2.5% by weight of the total composition.

Waterproofing agents, which can also act as binders, can be added to the composition to improve the weatherability of the composition. These are typically water insoluble compounds such as waxy materials and other hydrocarbons. Examples of suitable waterproofing agents are paraffin wax, stearate salts, beeswax, and similar compounds. One preferred wax compound is PAROWAX[®], available from Conros Corp.

of Scarborough, Ontario, Canada. Waterproofing agents can be incorporated into the composition in dry form, at about 5 to 12% by weight of the total composition.

It is also desirable to include within the composition taste altering compounds that render the composition unpalatable to animals, such as humans and pets. Exemplary compositions include those having a bitter taste. One such compound is commercially available as BITREX® from McFarlane Smith Ltd. of Edinburgh, Scotland. These compounds typically are added at a very low concentration. For example, a 0.1% BITREX solution can be added to the composition at about 1 to 2% by weight of the total composition.

Useful pH-affecting additives include calcium carbonate, potassium carbonate, potassium hydroxide, ascorbic acid, tartaric acid, and citric acid. Such additives may be used at a concentration in the range of about 0.2 to 5.0% by wt., and they should be effective to adjust the pH to within a range of about 5 to 9.

The molar ratio of the metal in the simple metal compound to the activity enhancing additive may be in the range of about 1:0.02 to 1:58. More preferably, this ratio is in the range of 1:0.3 to 1:12. Further, the metal in the simple metal compound may be present at a concentration range of about 200 to 20,000 ppm (0.02 to 2.0% by weight) while the activity enhancing additive may be present at a concentration in the range of about 2,000 to 60,000 ppm (0.2 to 6.0% by weight of the composition). One exemplary concentration range is about 0.1 to 0.5% by wt. of the composition for the metal and about 0.8 to 6.0% by wt. for the EDDS component.

Where the composition is used without a simple metal compound, i.e., in the form of a metal complex of EDDS, the metal complex can be present at 5000 to 90,000 ppm (0.5 to 9.0 % by wt.).

In one embodiment the composition may also include a co-active molluscicidal agent. One such co-active molluscicidal agent is metaldehyde. Other potential co-active

molluscicidal agents include methiocarb, carbaryl, isolan, mexcarbate, niclosamide, trifenmorph, carbofuran, anarcadic acid, and plant-derived saponins. Such co-active ingredients may be added to the composition at a concentration in the range of about 0.2 to 5.0% by wt.

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In yet another embodiment the composition may also include a fertilizer, such as virtually any plant fertilizer. Suitable fertilizers typically are granular and an example of one useful fertilizer is Ironite[®], available from Ironite Products Company of Scottsdale, Arizona. When present, fertilizers may be used at a concentration in the range of about 0.5 to 10.0% by weight of the composition.

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The composition of the invention typically is used in dry form and many of the constituent ingredients of the composition are included in dry form. However, it is often useful to include a sufficient amount of water within the composition to form a dough so that the ingredients can be more easily blended. Water is typically added at a concentration of about 15 to 60% by weight of the total composition. Water, however, typically is driven off by heating and drying the molluscicidal bait before it is used. The composition may also be formulated as a liquid, especially where the composition utilizes a metal complex of EDDS.

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As noted above, the composition of the present invention is typically used in a dry, spreadable form such as powders, granules, cubes, or pellets. The composition may be spread on or around areas infested by molluscs as well as in areas in which mollusc infestation is to be prevented. When used to combat aquatic molluscs the composition can simply be added to the environment inhabited by the molluscs.

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To prepare the composition, a suitable amount of the simple metal compound and the activity enhancing additive can be blended in dry form, with a dry carrier material. Thereafter, other dry ingredients (such as phagostimulants and waterproofing agents) are blended and mixed with the bait. Next, suitable amounts of liquid additives (such as preservatives, taste altering additives and water) are added to the dry mixture to form a

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dough. The bait can be covered, such as with a plastic wrap, and heated. One preferred heating technique is by heating in a microwave oven for 30 seconds to 10 minutes. After heating, the dough can be processed in a food grinder to obtain strands of the molluscicidal composition. This material is then dried, at elevated or ambient temperatures, and it can be made into a desired form, such as powder, pellets or granules.

One exemplary molluscicidal composition can be prepared as follows. First, metal compounds, e.g. iron carbohydrate or iron salts, are dry blended into a cereal flour (wheat) at between 1000 to 20,000ppm metal wt/wt. Dry EDDS, or its sodium salt, is then added to the flour on a molar level to the amount of iron added. This level can vary in the range of a metal:EDDS molar ratio in the range of about 1:0.02 to 1:58 ratio. The EDDS is added to the mixture while continually stirring. Other ingredients can be added to the mixture, such as, anti-microbials (Legend[®]), waterproofing agents, and phagostimulants (e.g., sugar). Water soluble additives are dissolved in water and then the water is blended into the dry wheat/iron compounds plus EDDS mixture. The dough is thoroughly mixed in a grinding device and extruded in the form of noodles. The resultant bait is dried at 40 degrees Celsius for 24 hours before testing.

The metal complexes can be synthesized by combining virtually any soluble metal compound, such as ferrous sulfate, with soluble EDDS or virtually any soluble derivative of EDDS. Following this combination, the pH can be adjusted (e.g., in the range of about 5 to 9) with a suitable agent such as a concentrated solution of potassium hydroxide. Exemplary metal compounds include reduced elemental iron, metal proteins (e.g., iron proteins, copper proteins, zinc proteins, aluminum proteins), metal salts (e.g., iron salts, copper salts, zinc salts, aluminum salts and mixtures thereof), metal carbohydrates (e.g., iron carbohydrates, copper carbohydrates, zinc carbohydrates, aluminum carbohydrates and mixtures thereof). Specific examples of such compounds include iron acetate, iron chloride, iron phosphate, iron phosphate/sodium citrate mixture, sodium iron phosphate, iron pyrophosphate, iron nitrate, iron ammonium sulfate, iron sulfide, iron albuminate, iron choline citrate, iron glycerol phosphate, iron citrate, iron ammonium citrate, iron fumarate,

iron gluconate, iron lactate, iron saccharate, iron fructate, iron dextrate, iron succinate, iron tartrate, copper acetate, copper chloride, copper phosphate, copper pyrophosphate, copper nitrate, copper ammonium sulfate, copper albuminate, copper sulfate, copper gluconate, copper lactate, copper saccharate, copper fructate, copper dextrate, zinc acetate, zinc chloride, zinc phosphate, zinc pyrophosphate, zinc nitrate, zinc ammonium sulfate, zinc albuminate, zinc sulfate, zinc gluconate, zinc lactate, zinc saccharate, zinc fructate, zinc dextrate, aluminum acetate, aluminum chloride, aluminum phosphate, aluminum pyrophosphate, aluminum nitrate, aluminum ammonium sulfate, aluminum albuminate, aluminum sulfate, aluminum gluconate, aluminum lactate, aluminum saccharate, aluminum fructate, and aluminum dextrate. Exemplary derivatives of EDDS include isomers of ethylene diamine disuccinic acid, salts of ethylene diamine disuccinic acid, including alkali earth, alkali metal, ammonium, substituted ammonium, mixtures of these salts, metal complexes of ethylene diamine disuccinic acid and mixtures thereof.

The following non-limiting examples serve to further illustrate the present invention.

Example 1

A tub test was set up with 20 *Deroceras reticulatum* and two lettuce plants per tub with three tubs per iron treatment and two tubs for controls. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
i r o n p/EDDS	DSA14/79/1 - 2800 ppm iron as iron phosphate plus 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour
Control	R4/118/1 - Control bait made with flour and sugar (94:6)*

* Unless otherwise noted, controls made with flour and sugar contain 94 parts flour and 6 parts sugar.

The tubs were kept in the greenhouse during assessment period. Data was collected at three and seven days after treatment, and the results obtained are shown below in Tables 1 and 2.

Table 1. Observations on mortality at 3 DAT*

Treat.	REP1	REP2	REP3
iron p/EDDS	7/20, bait readily eaten, very light plant feeding	6/20, 1 missing, bait readily eaten; very light plant feeding	7/20, bait readily eaten; no plant feeding
Control	0/20, light plant feeding	1/20, light plant feeding	na

*DAT = Days After Treatment

Table 2. Observations on mortality at 7 DAT.

Treat.	REP1	REP2	REP3	Total % Kill
iron p/EDDS	9/13, no more plant feeding	8/14 no more plant feeding	9/13 no more plant feeding	46/60, 76.7%
Control	2/20, heavy plant feeding	1/19, heavy plant feeding	na	4/40, 10.0%

Example 2

A tub test was set up with 15 *Deroceras reticulatum* and two lettuce plant per tub with two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Iron EDDS was synthesized from EDDS and iron chloride. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
iron EDDS 2000	R4/122/1 - 2000 ppm iron as iron EDDS, 6.0% sugar and balance of wheat flour
iron EDDS 2400	R4/122/2 - with 2400 ppm iron as iron EDDS, 6.0% sugar and balance of wheat flour
iron EDDS 2800	R4/122/3 with 2800 ppm iron as iron EDDS, 6.0% sugar and balance of wheat flour
Control	R4/118/1- Control bait made with flour and sugar

The tubs were kept in the greenhouse during assessment period. Data was collected at three and six days after treatment, and the results obtained are shown below in Tables 3 and 4.

Table 3. Observations on mortality at 4 DAT

Treat.	REP1	REP2
iron EDDS 2000	3/15, slight plant feeding	3/15, slight plant feeding
iron EDDS 2400	4/15, no plant feeding	11/15, no plant feeding
iron EDDS 2800	9/15, no plant feeding	6/15, slight plant feeding
Control	0/15	0/15

Table 4. Observations on mortality at 6 DAT

Treat.	REP1	REP2	Total % Kill
iron EDDS 2000	4/12	0/12	10/30, 33.3%
iron EDDS 2400	1/11	2/4	18/30, 60.0%
iron EDDS 2800	0/6	4/9	19/30, 63.3%
Control	0/15	0/15	0/30, 0%

Example 3

A tub test was set up with 15 *Deroceras reticulatum*, two lettuce plant per tub and two tubs per treatment, except for the aluminum nitrate treatment which had one replicate of 22 slugs. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tubs were kept outside during the duration of the experiment. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
10A	R4/123/1 - 2800 ppm Cu as Cu acetate and 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour
10B	R4/123/2 - 2800 ppm Cu as Cu chloride and 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour
10C	R4/123/3 - with 2800 ppm Cu as Cu oxide and 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour
10D	R4/123/6 - 2800 ppm Zn as Zinc chloride and 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour
10E	R4/122/3 - with 2800 ppm iron as iron phosphate and 10,800 ppm EDDS
10F	R4/118/1 - Control bait made with flour and sugar
10G	R4/123/5 - with 2800 ppm Al as Al nitrate and 10,800 ppm EDDS, 6.0% sugar and balance of wheat flour

The tubs were kept in the greenhouse during assessment period. Data was collected at three and seven days after treatment, and the results obtained are shown below in Tables 5 and 6.

Table 5. Observations on mortality at 3 DAT

Treat.	REP1	REP2
10A	0/15, no plant feeding	2/15, no plant feeding
10B	0/15, both plants eaten	2/15, 1 plant eaten
10C	1/15, medium plant feeding	1/15, light plant feeding
10D	2/15, light plant feeding	2/15, light plant feeding
10E	7/15, no plant feeding	5/17, no plant feeding
10F	1/15	0/15
10G	0/22, both plants eaten	na

Table 6. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
10A	3/15	3/11*	8/28, 28.6%
10B	0/15	1/13	3/30, 10.0%
10C	0/14	2/14	4/30, 13.3%
10D	3/13	1/13	8/30, 28.6%
10E	7/8	10/12	29/32, 90.1%
10F	0/14	1/15	2/30, 6.6%
10G	4/22	na	4/22, 18.2%

* = 2 slugs missing

Example 4

A test tub was set up with two replicates per treatment of 10 *Arion ater*. Two lettuce plants were placed per tub. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 5 grams of bait. Tubers were kept outside during the experimental period. The baits were made by dissolving the sodium EDDS and iron sugar in water, adding the flour and then adjusting the pH with K₂CO₃. Tubers were kept outside during the duration of the experiment. Baits of the type noted in the table below were made the day prior to use.

8A	R4/139/1, 0.28% iron (iron sugar) + 1.08% NaEDDS, pH 7.33
8B	R4/139/2, 0.28% iron (iron sugar) + 1.08% NaEDDS, pH 8.45
8C	R4/139/3, 0.28% iron (iron sugar) + 1.08% NaEDDS, pH 9.53
8D	R4/139/4, 0.28% iron (iron sugar) + 1.08% NaEDDS, pH 10.5
8E	R4/139/5, 0.28% iron (iron sugar) + 1.08% NaEDDS, not premixed
8F	DSA/120/1, Control bait made with flour and sugar

The tubs were kept outside during the assessment period. Data was collected at four and six days after treatment, and the results obtained are shown below in Tables 7 and 8.

Table 7. Observations on mortality at 4 DAT

Treat.	REP1	REP2
8A	0/10, bait 55% gone, no plant feeding	1/10, bait 100% gone, no plant feeding
8B	0/10, bait 100% gone, no plant feeding	0/10, bait 100% gone, medium plant feeding
8C	0/10, bait 70% gone, heavy plant feeding	0/10, bait 100% gone, heavy plant feeding
8D	0/10, bait 5.0% gone, heavy plant feeding	0/10, bait 5% gone, medium plant feeding
8E	1/10, bait 100% gone, light plant feeding	0/10, bait 100% gone, medium plant feeding
8F	0/10	0/10

Table 8. Observations on mortality at 6 DAT.

Treat.	REP 1	REP2	Total % Kill
8A	7/10	5/9	13/20, 65.0%
8B	8/10	5/10	13/20, 65.0%
8C	8/10	5/10	13/20, 65.0%
8D	0/10	1/10	1/20, 5.0%
8E	6/9	6/10	13/20, 65.0%
8F	0/10	0/10	0/20, 0.0%

Example 5

A test tub was set up with two replicates per treatment of 10 *Arion ater*. One large cabbage plant was placed per tub. Compost soil was used to cover the tub bottoms. Slugs were collected from the field, and added to the tubs along with 5 grams of bait.

Tubs were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

7A	R4/138/4, 2800 ppm iron as iron phosphate + 1.08% EDDS
7B	R4/140/1, 2800 ppm iron as iron phosphate + 2.5% EDDS
7C	R4/138/1, 4000 ppm iron as iron phosphate + 2.5% EDDS
7D	R4/138/2, 4500 ppm iron as iron phosphate + 2.5% EDDS
7E	DSA/120/1, Control bait made with flour and sugar

The tubs were kept outside during the assessment period. Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 9 and 10.

Table 9. Observations on mortality at 4 DAT

Treat.	REP1	REP2
7A	2/10, no plant feeding, most bait gone	3/10, med plant feeding, lots bait left
7B	5/10, no plant feeding, most bait gone	5/10, light plant feeding, most bait gone
7C	5/10, heavy plant feeding, lots bait left	8/10, heavy plant feeding, some bait left
7D	7/10, no plant feeding, lots bait left	6/10, no plant feeding, lots bait left
7E	0/10	0/10

Table 10. Observations on mortality at 7 DAT

Treat.	REP 1	REP2	Total % Kill
7A	7/8	4/7	16/20, 80.0%
7B	3/5	3/5	16/20, 80.0%
7C	3/5	1/2	17/20, 85.0%
7D	3/3	1/4	17/20, 85.0%
7E	0/10	0/10	0/20, 0.0%

Example 6

A standard tub test was set up with 15 *Deroceras reticulatum* and one lettuce plant per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tubs were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
6A	R4/155/1, 0.28 % iron as iron phosphahate and 1.50 % EDDS
6B	R4/155/2, 0.28 % iron as iron phosphahate and 1.75 % EDDS
6C	R4/153/1, 0.28 % iron as iron phosphahate and 2.25 % EDDS
6D	R4/155/3, 0.28 % iron as iron phosphahate and 2.75 % EDDS
6E	R4/140/2, 0.28 % iron a as iron phosphahate and 3.00 % EDDS
6F	R4/120/1 Control bait made with flour and sugar

Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 11 and 12.

Table 11. Observations on mortality at 4 DAT

Treat.	REP1	REP2
6A	2/15	1/15
6B	4/15	4/15
6C	2/15	0/15
6D	2/15	1/15
6E	1/15	1/15
6F	0/15	0/16

Table 12. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
6A	4/13	4/14	11/30, 36.7 %
6B	2/11	9/11	19/30, 63.3 %
6C	5/13	7/15	14/30, 46.7 %
6D	7/13	3/14	13/30, 43.3 %
6E	5/14	3/14	10/30, 33.3 %
6F	1/15	0/16	1/31, 3.3 %

Example 7

A standard tub test was set up with 15 *Deroceras reticulatum* and one lettuce plant per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tub s were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
5A	R4/154/1, iron phosphate/EDDS in a 50:50 bait of bonemeal: flour
5B	R4/154/2, iron phosphate/EDDS in a 90:10 bait of bonemeal: flour
5C	R4/143/3 Control bait made with flour and sugar

Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 13 and 14.

Table 13. Observations on mortality at 4 DAT

Treat.	REP1	REP2
5A	6/15	3/15
5B	2/15	4/14**
5C	0/15	0/15

** = 1 missing slug

Table 14. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
5A	7/9	8/12	24/30, 80.0 %
5B	5/13	7/10	18/29, 62.1 %
5C	0/15	0/15	0/30, 0.0 %

Example 8

A standard tub test was set up with 15 *Deroceras reticulatum* and one lettuce plant per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tubs were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
4A	R4/159/1, 0.28 % iron as iron sugar with 2.25 % EDDS
4B	R4/159/2, 0.28 % iron as iron gluconate with 2.25 % EDDS
4C	R4/159/3, iron phosphate plus 2.25 % EDDS plus 0.5 % sodium gluconate
4D	R4/159/4, iron phosphate plus 2.25 % EDDS plus 0.5 % calcium citrate
4E	R4/153/1, iron phosphate plus 2.25 % EDDS
4F	R4/143/3 Control bait made with flour and sugar

Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 15 and 16.

Table 15. Observations on mortality at 4 DAT

Treat.	REP1	REP2
4A	8/15	5/15
4B	2/15	2/15
4C	1/15	1/15
4D	0/15	1/15
4E	5/15	2/15
4F	0/15	0/15

Table 16. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
4A	4/7	5/10	23/30, 76.7 %
4B	5/13	9/13	18/30, 60.0 %
4C	1/14	3/13, 1 missing	6/29, 20.7 %
4D	6/15	4/14	11/30, 36.7 %
4E	3/10	na	7/15, 46.7 %
4F	0/15	0/15	0/30, 0.0 %

Example 9

A standard tub test was set up with 10 *Arion ater* and one lettuce plant per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 6 grams of bait and two cabbage plants. Tubs were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
3A	R4/161/1, 0.28% iron as iron sugar with 2.25 % EDDS
3B	R4/161/6, 0.28% iron as iron sulfate with 2.25 % EDDS
3C	R4/161/4, 0.28% iron as iron EDDS made from iron lactate
3D	R4/156/1, 0.28% iron as iron EDDS made from iron sulfate
3E	R4/143/3 Control bait made with flour and sugar

Data was collected at six days after treatment, and the results obtained are shown below in Table 17.

Table 17. Observations on mortality at 6 DAT

Treat.	REP1	REP2	Total % Kill
3A	10/10, no plant feeding	7/10, very light plant feeding	17/20, 85.0 %
3B	9/10, very light plant feeding	6/10, light plant feeding	15/20, 75.0 %
3C	3/10, no plant feeding	3/10, no plant feeding	6/20, 30.0 %
3D	4/10, no plant feeding	1/10, no plant feeding	5/20, 25.0 %
3E	0/10	0/10	0/20, 0.0 %

Example 10

A standard tub test was set up with 15 *Deroceras reticulatum* and two lettuce plants per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tubers were kept outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
2A	R4/164/2, 0.28 % iron as iron sulfate with 2.25 % EDDS at pH 3.58
2B	R4/167/1, 0.28 % iron as iron sulfate with 2.25 % EDDS at pH 5.54
2C	R4/167/2, 0.28 % iron as iron sulfate with 2.25 % EDDS at pH 7.34
2D	R4/167/3, 0.28 % iron as iron sulfate with 2.25 % EDDS at pH 9.30
2E	R4/167/4, 0.28 % iron as iron sulfate with 2.25 % EDDS at pH 9.78
2F	R4/162/2, 0.28 % iron as iron phosphate with 2.25 % EDDS
2G	R4/162/1 Control bait made with flour and sugar

Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 18 and 19.

Table 18. Observations on mortality at 4 DAT

Treat.	REP1	REP2
2A	6/16, no plant feeding	6/16, no plant feeding
2B	5/15, no plant feeding	7/15, no plant feeding
2C	5/15, no plant feeding	6/15, no plant feeding
2D	5/15, no plant feeding	4/15, no plant feeding
2E	2/15, no plant feeding	1/15, no plant feeding
2F	1/15, no plant feeding	2/15, light plant feeding
2G	0/15	0/15

Table 19. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
2A	6/10	8/10	26/30, 86.7 %
2B	7/10	7/8	26/30, 86.7 %
2C	8/10	7/9	26/30, 86.7 %
2D	4/10	7/11	20/30, 66.7 %
2E	5/13	7/14	15/30, 50.0 %
2F	7/14	8/13	18/30, 60.0 %
2G	0/15	0/15	0/30, 0.0 %

Example 11

A standard tub test was set up with 15 *Deroceras reticulatum* and one lettuce and one cabbage plant per tub and two tubs per treatment. Compost soil was used to cover the tub bottoms. Slugs were collected from the field and added to the tubs along with 2 grams of bait. Tubs were kept in a outside during the experimental period. Baits of the type noted in the table below were made the day prior to use.

Code	Bait
1A	R4/170/1, 0.28% iron as Fe II sulfate with 2.25 % EDDS
1B	R4/170/2, 0.15% iron as Fe II sulfate with 2.25 % EDDS
1C	R4/164/2, 0.28% iron as Fe III sulfate with 2.25 % EDDS
1D	R4/170/3, 0.28% iron as iron sugar (10%) with 2.5 % EDDS
1E	R4/161/1, 0.28% iron as iron sugar (20%) with 2.5 % EDDS
1F	R4/162/2, 0.28% iron as Fe III phosphate with 2.25 % EDDS
1G	R4/162/1 Control bait made with flour and sugar

Data was collected at four and seven days after treatment, and the results obtained are shown below in Tables 20 and 21.

Table 20. Observations on mortality and plant feeding at 4 DAT

Treat.	REP1	REP2
1A	3/15, no plant feeding	3/15, no plant feeding
1B	2/15, no plant feeding	3/15, no plant feeding
1C	3/15, no plant feeding	1/15, no plant feeding
1D	3/15, no plant feeding	5/15, no plant feeding
1E	5/15, no plant feeding	4/15, no plant feeding
1F	2/15, no plant feeding	1/15, no plant feeding
1G	0/15	0/15

Table 21. Observations on mortality at 7 DAT

Treat.	REP1	REP2	Total % Kill
1A	9/12	7/12	22/30, 73.3 %
1B	9/13	7/12	21/30, 70.0 %
1C	10/12	11/14	25/30, 83.3 %
1D	11/12	8/10	27/30, 90.0 %
1E	8/10	6/11	23/30, 76.7 %
1F	6/13	5/14	14/30, 46.7 %
1G	0/15	1/15	1/30, 3.3 %

Having described the preferred embodiments of the invention, it will be apparent to one of ordinary skill in the art that other embodiments incorporating their concepts may be used. It is believed, therefore, that these embodiments should not be limited to disclosed embodiments but rather should be limited only by the spirit and scope of the appended claims. All publications and references cited herein are expressly incorporated herein by reference in their entirety. Unless otherwise noted, all percentages by weight are percent of the total composition.

What is claimed is:

1. A mollusc stomach poison composition, comprising:

a simple metal compound, including metals selected from the group consisting of iron, copper, zinc aluminum and mixtures thereof;

an activity enhancing additive selected from the group consisting of ethylene diamine disuccinic acid, isomers of ethylene diamine disuccinic acid, salts of ethylene diamine disuccinic acid, metal complexes of ethylene diamine disuccinic acid and mixtures thereof; and

a carrier material edible to molluscs,
the mollusc stomach poison being effective to kill molluscs upon ingestion by molluscs.

2. The composition of claim 1, wherein the salt of ethylene diamine disuccinic acid is selected from the group consisting essentially of alkali metal salts, alkali earth salts, ammonium salts, substituted ammonium salts, and mixtures thereof.

3. The composition of claim 1, further comprising a molluscicidal co-active ingredient.

4. The composition of claim 3, wherein the molluscicidal co-active ingredient is selected from the group consisting of metaldehyde, methiocarb, carbaryl, isolan, mexcarbate, mercaptodimethur, niclosamide, trifenmorph, carbofuran, anarcadic acid, plant-derived saponins, and mixtures thereof.

5. The composition of claim 1, further comprising a pH-adjusting agent.

6. The composition of claim 5, wherein the pH-adjusting agent is selected from the group consisting of calcium carbonate, potassium carbonate, potassium hydroxide, ascorbic acid, tartaric acid, and citric acid.

7. The composition of claim 5, wherein the pH is in the range of about 5 to 9.
8. The composition of claim 1, wherein the molar ratio of the metal to the bait additive is in the range of about 1:0.02 to 1:58.
- 5 9. The composition of claim 1, wherein the metal is present in the simple metal compound at a concentration in the range of about 200 to 20,000 ppm.
- 10 10. The composition of claim 1, wherein the activity enhancing additive is present at a concentration in the range of about 0.2 to 6.0 percent by wt. of the composition.
11. The composition of claim 1, wherein the carrier is a mollusc food.
12. The composition of claim 11, wherein the mollusc food is selected from the group consisting of wheat flour, wheat cereal, agar, gelatin, oil cake, pet food wheat, soya, oats, corn, citrus mash, rice, fruits, fish by-products, sugars, coated vegetable seeds, coated cereal seeds, casein, blood meal, bone meal, yeast, fats, beer products, and mixtures thereof.
- 15 13. The composition of claim 11, wherein the mollusc food is a bone meal - wheat flour mixture having a ratio of bone meal to wheat flour in the range of 50:50 to 90:10.
- 20 14. The composition of claim 1, wherein the simple metal compound is selected from the group consisting of reduced elemental iron, iron proteins, iron salts, iron carbohydrates, copper proteins, copper salts, copper carbohydrates, zinc proteins, zinc salts, zinc carbohydrates, aluminum proteins, aluminum salts, aluminum carbohydrates, and mixtures thereof.
- 25

15. The composition of claim 14, wherein the simple metal compound is selected from the group consisting of iron acetate, iron chloride, iron phosphate, iron phosphate/sodium citrate mixture, sodium iron phosphate, iron pyrophosphate, iron nitrate, iron ammonium sulfate, iron albuminate, iron sulfate, iron sulfide, iron choline citrate, iron glycerol phosphate, iron citrate, iron ammonium citrate, iron fumarate, iron gluconate, iron lactate, iron saccharate, iron fructate, iron dextrate, iron succinate, iron tartrate, copper acetate, copper chloride, copper phosphate, copper pyrophosphate, copper nitrate, copper ammonium sulfate, copper albuminate, copper sulfate, copper gluconate, copper lactate, copper saccharate, copper fructate, copper dextrate, zinc acetate, zinc chloride, zinc phosphate, zinc pyrophosphate, zinc nitrate, zinc ammonium sulfate, zinc albuminate, zinc sulfate, zinc gluconate, zinc lactate, zinc saccharate, zinc fructate, zinc dextrate, aluminum acetate, aluminum chloride, aluminum phosphate, aluminum pyrophosphate, aluminum nitrate, aluminum ammonium sulfate, aluminum albuminate, aluminum sulfate, aluminum gluconate, aluminum lactate, aluminum saccharate, aluminum fructate, and aluminum dextrate.

16. A composition, comprising:

a fertilizer material; and

an environmentally compatible molluscicidal composition, including

a simple metal compound, having metals selected from the group consisting of iron, copper, zinc or aluminum and mixtures thereof, an activity enhancing additive selected from the group consisting of ethylene diamine disuccinic acid, isomers of ethylene diamine disuccinic acid, salts of ethylene diamine disuccinic acid, metal complexes of ethylene diamine disuccinic acid and mixtures thereof, and a carrier material edible to molluscs,

the mollusc stomach poison being effective to kill molluscs upon ingestion by molluscs.

17. The composition of claim 16, wherein the fertilizer is a granular fertilizer.

18. An ingestible molluscicidal composition, comprising:

a metal compound selected from the group consisting of ferric ethylene diamine
disuccinic acid, ferrous ethylene diamine disuccinic acid, copper ethylene diamine
disuccinic acid, zinc ethylene diamine disuccinic acid, aluminum ethylene diamine
disuccinic acid, and mixtures thereof; and

a carrier material edible to molluscs.

19. The composition of claim 18, wherein the carrier material is a mollusc food.

20. The composition of claim 18, further comprising a co-active molluscicidal agent.

21. The composition of claim 20, wherein the co-active molluscicidal agent is selected from the group consisting of metaldehyde, methiocarb, carbaryl, isolan, mexcarbate, mercaptodimethur, niclosamide, trifenmorph, carbofuran, anarcadic acid, plant-derived saponins, and mixtures thereof.

22. The composition of claim 18, wherein the metal is present in the metal compound at a concentration in the range of about 0.5 to 9.0 percent by wt. of the composition.

23. The composition of claim 18, further comprising a fertilizer material.

24. A method of exterminating unwanted mollusc pests, comprising the steps of:
providing a molluscicidal composition including

a simple metal compound, including metals selected from the group consisting of iron, copper, zinc or aluminum and mixtures thereof,
an activity enhancing additive selected from the group consisting of ethylene diamine disuccinic acid, isomers of ethylene diamine disuccinic

acid, salts of ethylene diamine disuccinic acid, metal complexes of
ethylene diamine disuccinic acid and mixtures thereof, and
a carrier material edible to molluscs;

applying the molluscicidal composition to an area infested with molluscs; and
allowing the molluscs to ingest the molluscicidal composition.

25. A method of exterminating unwanted mollusc pests, comprising the steps of:
providing a molluscicidal composition including

a metal compound selected from the group consisting of ferric ethylene
diamine disuccinic acid, ferrous ethylene diamine disuccinic acid,
copper ethylene diamine disuccinic acid, zinc ethylene diamine
disuccinic acid, aluminum ethylene diamine disuccinic acid, and
mixtures thereof, and

a carrier material edible to molluscs;

applying the molluscicidal composition to an area infested with molluscs; and
allowing the molluscs to ingest the molluscicidal composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/00740

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N25/00 A01N37/44 C05G3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N C05G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 26789 A (YOUNG COLIN LESLIE) 31 July 1997 see page 6, line 13 - page 11, line 3 & AU 77420 98 A cited in the application	1-25
Y	DE 195 18 150 A (CIBA GEIGY AG) 21 November 1996 see page 2, line 5 - line 10	1-25
Y	WO 96 05728 A (NEUDORFF W GMBH KG) 29 February 1996 see page 3, line 3 - line 37 see page 5, line 14 - line 20 & US 5 437 870 A cited in the application	1,11,13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "P" document published prior to the international filing date but later than the priority date claimed

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

9 June 1999

Date of mailing of the international search report

23/06/1999

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INTERNATIONAL SEARCH REPORT

International Application No
 PCT/EP 99/00740

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT.

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Section Ch, Week 7820 Derwent Publications Ltd., London, GB; Class C03, AN 78-35955A XP002105435 & JP 53 038624 A (CHUGAI PHARM CO LTD) , 8 April 1978 see abstract -----	16-18, 23
A	DATABASE CROPU STN-International STN-accession no. 90-84412, I.F.HENDERSON ET AL.: "Control of Slugs with Contact-Action Molluscicides" XP002105433 see abstract & ANN.APPL..BIOL., vol. 116, no. 2, 1990, pages 273-278, -----	1-25
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/00740

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8/8 - (C) FILE CAPLUS
 STN CA Caesar accession number : 1405
 AN - 1970:474314 CAPLUS
 DN - 73:74314
 TI - Effect of a chelating agent (EDTA) on the tobacco hornworm
 IN - Terranova, Andrew C.; Callenbach, J. C.
 CS - Metab. and Radiat. Res. Lab., Agr. Res. Serv., Fargo, ND, USA
 SO - Journal of Economic Entomology (1970), 63(3), 886-91
 CODEN: JEENAI; ISSN: 0022-0493
 DT - Journal
 LA - English
 AN - 1970:474314 CAPLUS
 DN - 73:74314
 ED - Entered STN: 12 May 1984
 TI - Effect of a chelating agent (EDTA) on the tobacco hornworm
 IN - Terranova, Andrew C.; Callenbach, J. C.
 CS - Metab. and Radiat. Res. Lab., Agr. Res. Serv., Fargo, ND, USA
 SO - Journal of Economic Entomology (1970), 63(3), 886-91
 CODEN: JEENAI; ISSN: 0022-0493
 DT - Journal
 LA - English
 CC - 9 (Nonmammalian Biochemistry)
 AB - Several adverse effects were obsd. in developing *Manduca sexta*, fed on a diet contg. the tetrasodium salt of EDTA. Delayed development, paralysis, molting difficulties, morphol. abnormalities, and mortality were some of the effects noted. These effects were influenced not only by the concn of EDTA in the diet but also by the length of time the larvae were fed on the diet.
 ST - tobacco hornworm EDTA; hornworm tobacco EDTA; EDTA tobacco hornworm; *Manduca* insecticide EDTA
 IT - Protoparce
 (*sexta*, EDTA effect on)
 IT - 64-02-8
 RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)
 (Protoparce *sexta* response to)

XP-002265347

